FCT

Top-down uncertainty evaluations
Difficulties and solutions

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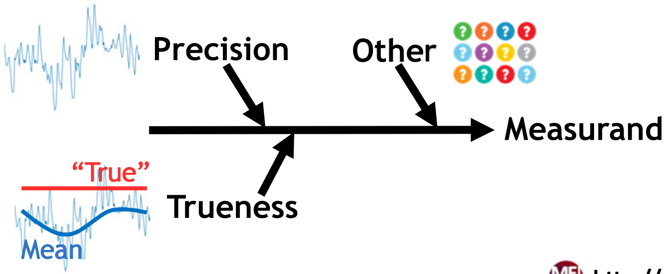

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Outline

1. Approaches for uncertainty evaluation
2. Top-down approach based on intralaboratory data
3. Variation of the uncertainty with the concentration
4. Application example
5. Conclusions

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1. Approaches for uncertainty evaluation

Bottom-up approach

Top-down approach based on intralaboratory data

Top-down approach based on interlaboratory data

1. Approaches for uncertainty evaluation

Bottom-up approach

Top-down approach based on intralaboratory data

Top-down approach based on interlaboratory data

2. Top-down approach based on intralaboratory data

Uncertainty components are quantified in three groups:

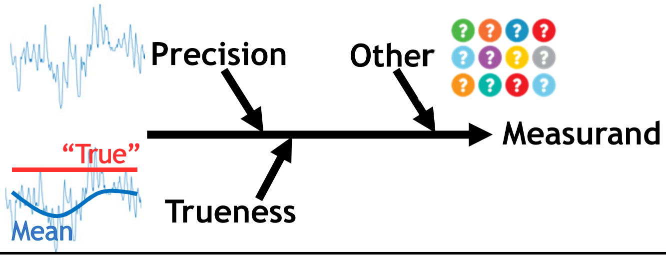
Precision (random effects observed in different days):

» Quantified by the intermediate precision standard deviation

Trueness (systematic effects observed between days)

» Quantified from deviations observed from the analysis of samples with a reference concentration

Others components



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2. Top-down approach based on intralaboratory data

The three components are combined using the law of propagation of uncertainty:

As absolute standard uncertainties (with concentration units):

$$U = k\sqrt{u_P^2 + u_T^2 + u_O^2}$$

As relative standard uncertainties (unitless):

$$U = kc\sqrt{u'^2_P + u'^2_T + u'^2_O}$$

k - coverage factor;

U - expanded uncertainty.

where u_P and u'_P, u_T and u'_T, and u_O and u'_O are absolute and relative precision, trueness and other standard uncertainties.

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2. Top-down approach based on intralaboratory data

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As absolute standard uncertainties (with concentration units):

$$U = k\sqrt{u_{\mathrm{P}}^2 + u_{\mathrm{T}}^2 + u_{\mathrm{O}}^2}$$

As relative standard uncertainties (unitless):

$$U = kc\sqrt{u'^2_{\mathrm{P}} + u'^2_{\mathrm{T}} + u'^2_{\mathrm{O}}}$$

where u_{P} and u'_{P}, u_{T} and u'_{T}, and u_{O} and u'_{O} are absolute and relative precision, trueness and other standard uncertainties.

u_{P} or u'_{P} are estimated by the absolute, s_{I}, or relative, s'_{I}, intermediate precision standard deviations.

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2. Top-down approach based on intralaboratory data

This approach relies on the randomisation of relevant environmental and operational conditions:

The following difficulties have to be understood and faced:

» The variation of measurement uncertainty with the concentration (applicable to data from few concentration levels);

» The impact of reference materials values uncertainty and measured concentration precision on systematic effects assessment;

Note: Avoid uncertainty underevaluation…

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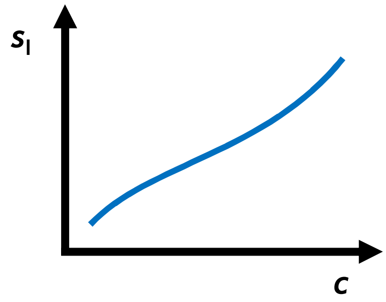
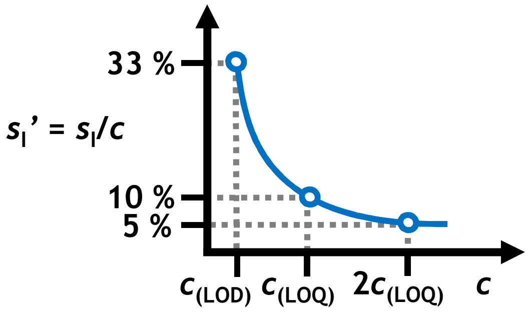
3. Variation of the uncertainty with the concentration

How the variation of the uncertainty with the concentration can be modelled? Regardless of the method:





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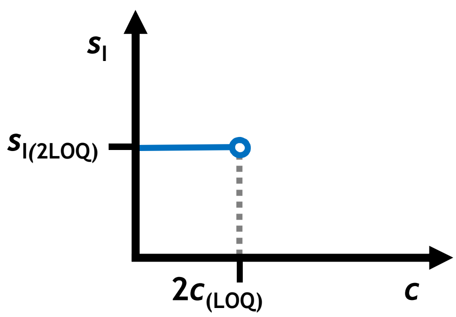
3. Variation of the uncertainty with the concentration

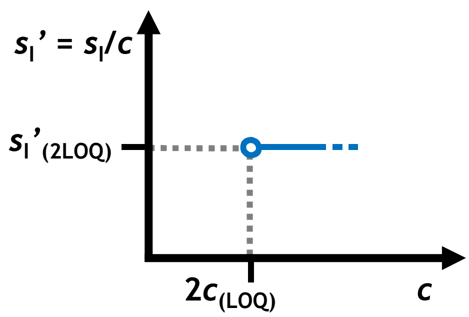
3.1. Precision uncertainty

(…) If s_I is estimated at $2c_{LOQ}$:

Interval I $[0, 2c_{LOQ}[$:



Interval II $[2c_{LOQ}, c_{MAX}[$:



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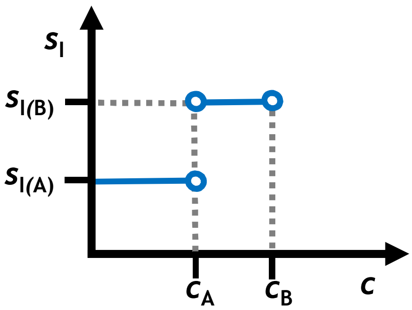
3. Variation of the uncertainty with the concentration

3.1. Precision uncertainty

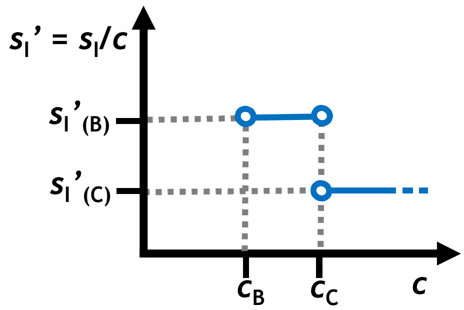
(...) If s_I is estimated at three concentrations c_A, c_B and c_C:

Example: $c_A < 2c_{LOQ} < c_B < c_C$:

Interval A $[0, c_B[$:



Interval B $[c_B, c_{Max}[$:



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3. Variation of the uncertainty with the concentration

3.2. Trueness uncertainty

Frequently, systematic effects are proportional to the concentration, being assessed from analyte recovery:

$$R_i = \frac{c_i}{c_{\mathrm{Ref}i}}$$

c_i - measured concentration
$c_{\mathrm{Ref}i}$ - reference concentration

The mean recovery, $\bar{R}$, is less affected by random effects:

$$\bar{R} = \sum_{i=1}^{N} \frac{c_i}{c_{\mathrm{Ref}i}} / N = \sum_{i=1}^{N} R_i / N$$

Mean recovery and respective uncertainty should be considered to decide if results should be corrected for observed mean recovery.

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3. Variation of the uncertainty with the concentration

3.2. Trueness uncertainty

Challenges:

How to estimate trueness from results of different and independent reference materials:

Example 1: Samples from various proficiency tests;

Example 2: Different samples with different native analyte and spiked at different levels.

How to handle cases were recovery is different for the various recovery tests.

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3. Variation of the uncertainty with the concentration

3.2. Trueness uncertainty

Challenges:

How to estimate trueness from results of diferent and independent reference materials:

Control what is going on!

Randomisation does not solve all problems

Example 2: Differen … nalyte and spiked at differe…

How to handle case … he various recovery tests.

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3. Variation of the uncertainty with the concentration

3.2. Trueness uncertainty

Samples from proficiency tests (each sample analysed once):

In proficiency test i (i = 1 to N):

$$R_i = \frac{c_i}{c_{\text{Ref}i}} \quad \text{and} \quad u(R_i) = R_i\sqrt{\left(\frac{s_{\text{I}}(c_i)}{c_i}\right)^2 + \left(\frac{u(c_{\text{Ref}i})}{c_{\text{Ref}i}}\right)^2}$$

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3. Variation of the uncertainty with the concentration

3.2. Trueness uncertainty

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Assess the metrological compatibility of pairs of recovery values:

(i-th and j-th PT; $i \neq j$)

$$|R_i - R_j| \leq 3\sqrt{u^2(R_i) + u^2(R_j)}$$

		PT Scheme	Round 1	Round 2	Round 3	Round 4	Round 5	Round 6	Round 7	Round 8	Round 9	Round 10	Round 11
		R_j	103.7%	110.0%	97.0%	95.8%	109.3%	101.4%	110.8%	111.8%	96.4%	100.3%	96.2%
PT Scheme	R_i	$u(R_i)$ or $u(R_j)$	8.8%	3.7%	3.8%	2.8%	9.3%	3.1%	3.2%	3.6%	3.0%	3.1%	2.9%
Round 1	103.7%	8.8%											
Round 2	110.0%	3.7%	E										
Round 3	97.0%	3.8%	E	E									
Round 4	95.8%	2.8%	E	D	E								
Round 5	109.3%	9.3%	E	E	E	E							
Round 6	101.4%	3.1%	E	E	E	E	E						
Round 7	110.8%	3.2%	E	E	E	D	E	E					
Round 8	111.8%	3.6%	E	E	E	D	E	E	E				
Round 9	96.4%	3.0%	E	E	E	E	E	E	D	D			
Round 10	100.3%	3.1%	E	E	E	E	E	E	E	E	E		
Round 11	96.2%	2.9%	E	E	E	E	E	E	D	D	E	E	
Round 12	95.8%	2.6%	E	D	E	E	E	E	D	D	E	E	E

E - Metrologically equivalent recoveries

D - Metrologically DIFFERENT recoveries

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3. Variation of the uncertainty with the concentration

3.2. Trueness uncertainty

(…) If are compatible (i.e. metrologically equivalent): $\bar{R} = \sum R_i / N$

$$u(\bar{R}) = \sqrt{\sum_{i=1}^{N} \left[R_i^2 \cdot u^2(R_i)\right] \Big/ N}$$

(…) If are NOT compatible:

$$u(\bar{R}) = \sqrt{\sum_{i=1}^{N} \left\{R_i^2 \left[\left(\frac{s_{R_i}}{R_i}\right)^2 + \left(\frac{u(c_{\mathrm{Ref}i})}{c_{\mathrm{Ref}i}}\right)^2\right]\right\} \Big/ N}$$

where s_{R_i} is recoveries standard deviation.

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3. Variation of the uncertainty with the concentration

3.2. Trueness uncertainty

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Assessment of the $\bar{R}$ (≅100 %)

$$\frac{|1 - \bar{R}|}{u(\bar{R})} \leq 2$$

yes (no correction)

no (correction, if allowed)

This decision has an impact on measurement traceability

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3. Variation of the uncertainty with the concentration

3.2. Uncertainty combination (*c* - measured concentration)

Interval I [0, 2c_{LOQ}[:$\langle \mathrm{I} \rangle$

$$U = 2\sqrt{s_{\mathrm{I}}^{2}\langle \mathrm{I} \rangle + \left(c \cdot u'(\bar{R})\right)^{2}}$$

Interval II [2c_{LOQ}, c_{MAX}[: $\langle \mathrm{II} \rangle$

$$U = 2c\sqrt{s'^{2}_{\mathrm{I}}\langle \mathrm{II} \rangle + u'^{2}(\bar{R})}$$

$u'(\bar{R}) = (u(\bar{R})/\bar{R})$

For *k* = 2 and a confidence level of approximately 95 %.

3. Variation of the uncertainty with the concentration

Summary of a simple case:

Intermediate precision, $s_{I(2LOQ)}$, estimated at 2c_{LOQ}

- Interval I [0, 2c_{LOQ}[: $u_P = s_{I(2LOQ)}$
- Interval II [2c_{LOQ}, c_{MAX}[: $u'_P = s'_{I(2LOQ)}$

PT	c_i	R_i	Interval	$s_i(c_i)$	$u(R_i)$
1	8.48	94.9%	I	0.68	8.5%
2	16.9	92.6%	II	1.4	7.7%
3	14.8	90.6%	I	1.2	8.0%
4	25.0	95.2%	II	2.0	8.0%
5	16.0	91.2%	II	1.3	8.0%
6	14.0	86.9%	I	1.1	7.8%
7	53.0	89.9%	II	4.2	8.1%
8	17.9	78.4%	II	1.4	6.7%
9	14.0	89.1%	I	1.1	7.6%
10	21.8	98.0%	II	1.7	8.5%
11	60.2	92.4%	II	4.8	7.7%

All R_i are equivalent

$\bar{R}$ is ≠ 100 %
(results should be corrected for recovery)

$c_{corr} = c/\bar{R}$

3. Variation of the uncertainty with the concentration

Summary of a simple case:

Intermediate precision, $s_{I(2LOQ)}$, estimated at $2c_{LOQ}$

Interval I $[0, 2c_{LOQ}[$: $u_P = s_{I(2LOQ)}$

Interval II $[2c_{LOQ}, c_{MAX}[$: $u'_P = s'_{I(2LOQ)}$

PT	c_i	R_i	Interval	$s_i(c_i)$	$u(R_i)$
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All R_i are equivalent

$\overline{R}$ is ≠ 100 % (results should be corrected for recovery)

$c_{corr} = c/\overline{R}$

Interval I $[0, 2c_{LOQ}[$:

$$U = 2\sqrt{s^2_{I(2LOQ)} + (c_{corr} \cdot u'(\overline{R}))^2}$$

Interval II $[2c_{LOQ}, c_{MAX}[$

$$U = 2c_{corr}\sqrt{s'^2_{I(2LOQ)} + u'^2(\overline{R})}$$

3. Variation of the uncertainty with the concentration

Summary of a simple case:

Measurement model:

- Applicable to a wide concentration interval;
- Adapts to the uncertainty of the reference value and precision of PT samples analysis;
- Takes the variation of recovery, not explained my measurement precision, into account.

This model can be improved for replicate sample analysis…

3. Variation of the uncertainty with the concentration

Note for Trueness Uncertainty determination:

Analysis of various samples with different native concentrations, c_{0i}, and spiked at different concentrations, c_{+i}.

$$\bar{R} = \sum_{i=1}^{N} \left(\frac{c_i - c_{0i}}{c_{+i}} \right) \Big/ N = \sum_{i=1}^{N} R_i \Big/ N$$

where c_i is the estimated concentration of the spiked sample i.

In this case, since c_i and c_{0i} are analysed under repeatability conditions:

$$u(\bar{R}) = \sqrt{\sum_{i=1}^{N} R_i^2 \left[\frac{s_\mathrm{r}^2(c_i) + s_\mathrm{r}^2(c_{i0})}{(c_i - c_{i0})^2} + \left(\frac{u(c_{+i})}{c_{+i}} \right)^2 \right] \Big/ N}$$

where s_r are repeatability standard deviations determined for interval I or II

4. Application examples

Determinations of total Cr, Cu, Li, Mn and Zn, and acid extractable Ni and Pb according to the EPA 3051A standard [1], in marine sediments [2].

1 - EPA, Method 3051A - Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, EPA, USA, 2007.
2 - C. Palma, V. Morgado, R. J. N. Bettencourt da Silva, Top-down evaluation of matrix effects uncertainty, Talanta 192 (2018) 278-28 7.

4. Application example

Element (procedure)	Cr (OSPAR)	Cu (OSPAR)	Li (OSPAR)	Mn (OSPAR)	Ni (EPA3051A)	Pb (EPA3051A)	Zn (OSPAR)
Matrix	Marine sediments						
c_{LOQ} (mg kg^{-1})	5	5	0.5	5	7.5	10	2
$u_P\langle I\rangle$(mg kg^{-1})	0.633	0.347	0.0675	0.680	1.18	1.08	0.159
$u'_P\langle II\rangle$(%)	6.33	3.47	6.75	6.80	7.97	6.37	3.97
u_T(absolute)	0.0189	0.0111	0.0395	0.0150	0.0131	0.0141	0.0145
$\bar{R}$ (%)	110	100	104	99.3	88.9	93.1	103
Is $\bar{R} \cong 100$ % ?	No	Yes	Yes	Yes	No	No	Yes
$u_c\langle I\rangle$(mg kg^{-1})	1.05	0.612	0.127	0.920	1.25	1.90	0.365
$u'_c\langle II\rangle$(%)	10.5	6.13	12.7	9.20	8.44	10.1	9.13
$U\langle I\rangle$(mg kg^{-1})	2.10	1.22	0.254	1.84	2.51	3.79	0.731
$U'\langle II\rangle$(%)	21.0	12.3	25.4	18.4	16.9	20.2	18.3
Compatibility external check (CEC)	20 in 20	20 in 20	15 in 15	20 in 20	20 in 20	20 in 20	20 in 20
$u_c^{tg}\langle I\rangle$(mg kg^{-1})	1.63	1.125	0.1125	0.675	1.44	2.25	1.500
$u'^{tg}_c\langle II\rangle$(%)	22.5	17.5	17.5	13.0	15.8	17.5	43.8

c_{LOQ} – Limit of Quantification in mass fraction units; CEC – number of estimated proficiency test results compatible with the reference value; $u_c^{tg}\langle I\rangle$ and $u'^{tg}_c\langle II\rangle$ – absolute and relative target standard uncertainties below and above $2w_{LOQ}$, respectively [4].

3 - QUASIMEME, Quasimeme Laboratory Performance Studies - Programme 2017, Wageningen University, Wageningen, 2017.
4 - Eurachem/CITAC Guide: Setting and Using Target Uncertainty in Chemical Measurement, 2015.

4. Application example

Element (procedure)	Cr (OSPAR)
Matrix	Marine sediments
c_{LOQ} (mg kg^{-1})	5
$u_P\langle I\rangle$(mg kg^{-1})	0.633
$u'_P\langle II\rangle$(%)	6.33
u_T(absolute)	0.0189
$\bar{R}$ (%)	110
Is $\bar{R} \cong 100$ % ?	No
$u_c\langle I\rangle$(mg kg^{-1})	1.05
$u'_c\langle II\rangle$(%)	10.5
$U\langle I\rangle$(mg kg^{-1})	2.10
$U'\langle II\rangle$(%)	21.0
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5. Conclusions

Developed top-down evaluation of the measurement uncertainty:

- **allows an easy modeling of uncertainty variation with the measured value**
- **was successfully applied to several measurements..**

CHEAP & EASY

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